

LOW VOLATILITY HALON FIRE EXTINGUISHING AGENTS
WITH REDUCED GLOBAL ENVIRONMENTAL IMPACTS

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ABSTRACT

The continuation of work, on non-volatile precursors (NVPs), including some new candidate agents which pyrolyze in the heat of a fire to generate Halon-like fire extinguishing agents, will be discussed.

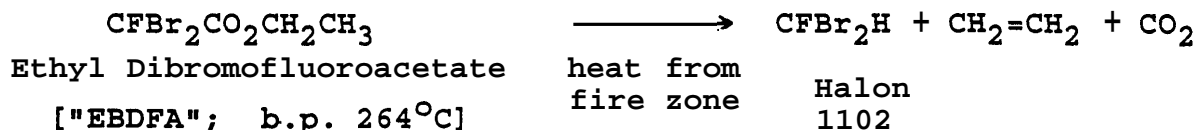
NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances.

LOW VOLATILITY HALON FIRE EXTINGUISHING AGENTS

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Within the past few years there has been much attention directed to possible drop-in replacements for Halon fire extinguishing agents which are now no longer in production, due to their unacceptable ozone depletion and global warming potentials [ODP, GWP]. Large stockpiles of Halons 1211 (CF_2BrCl ; b.p. -2.5°C), 1301 (CF_3Br ; b.p. -58°C), and to a lesser extent 2402 ($\text{CF}_2\text{BrCF}_2\text{Br}$, b.p. 47°C) are still maintained in the Halon bank, however, for future use on a prioritized basis for firefighting requirements. For total flood agent systems, one of the most promising high volatility candidates is trifluoromethyl iodide (CF_3I , b.p. $= -22^\circ$). For streaming and similar agent compositions requiring lower volatilities, a variety of fluorocarbon (e.g., C_6F_{14} , b.p. 60°) and hydrochlorofluorocarbon (e.g., HCFC 123 (CF_3CHCl_2 ; b.p. $= 27^\circ\text{C}$)) compositions have been tested and marketed. For streaming agent applications even the higher boiling of these compositions are still sufficiently volatile that very large amounts of such agents need to be delivered to a fire in order to ensure adequate extinguishing concentrations; most of the agent is lost in delivery to the fire zone. None of these agents enjoys the low toxicities provided by the Halons; and, particularly for the HCFC agent systems, moderate but probably eventually unacceptable ODP and GWP parameters pertain.

Since the poor deliverability and requirements for excessive dose delivery, and the high ODP, GWP and vapor toxicity problems are all due to the moderate to high volatilities of these compounds, we initiated an investigation of non-volatile precursor (NVP) fire-fighting agents which would degrade in the heat of fire to release analogs of conventional Halons. The first phase of project work, completed two years ago, involved the synthesis and study of several new compounds which decompose thermally to yield olefinic and hydrobromofluorocarbon (OBFC, HBFC) products. For example:

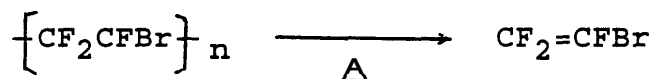


The compounds were tested for fire extinguishing efficiency at the US Air Force Wright Laboratories Fire Research Division at Tyndall Air Force Base, Florida [TAFB]. All of the compounds had good cup burner extinguishing values; two of the agents (including "EBDA", above) were actually superior in fire extinguishing performance to the Halons.

Moreover, since much less of these agents would be required for adequate extinguishment (due to the low volatility and loss due to evaporation en route to the fire) these would appear to be actually even more effective than the conventional Halons.

The compounds which were initially investigated were all liquid species of fairly simple molecular structure. The entire thrust of this study was to ascertain the general feasibility of thermal cracking of large molecules to afford gaseous Halon-like extinguishing agents in the heat of a fire. Although no toxicity studies were performed, it was understood that all of the initial agents would be unacceptably toxic, particularly in terms of ingestion or absorption through the skin. Having demonstrated, however, the general feasibility of this approach, attention was directed in the current research program to development of NVP fire extinguishing agents which would be safe, cheap and efficient. Such NVP agents would have greatly reduced ODP, GWP and toxic vapor properties, and would pose greatly reduced atmospheric emissions due to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances.

In the first phase of the current project, several polymers of bromofluoroolefins were synthesized, along with several bromofluoropolyesters. All but one of these agents were disappointing in terms of thermal gravimetric analysis (TGA) performance. One of the polyolefins, polybromotrifluoroethylene (PBTFE) exhibited a startlingly clean pyrolysis, with "unzipping" of the polymer providing almost quantitative production of the original olefin (bromotrifluoroethylene) by retropolymerization; see Figure 1.



Sample: POLY (BROMOTRIFLUOROETHYLENE) TGA File: Q DB8AN.02
 Size: 7.2260 mg Operator: PLC
 Method: 10°C/MIN TO 700°C Run Date: 26-Sep-94 11:39
 Comment: PT PAN N2 PURGE BALANCE = 42ml/MIN FURNACE =57ml/MIN

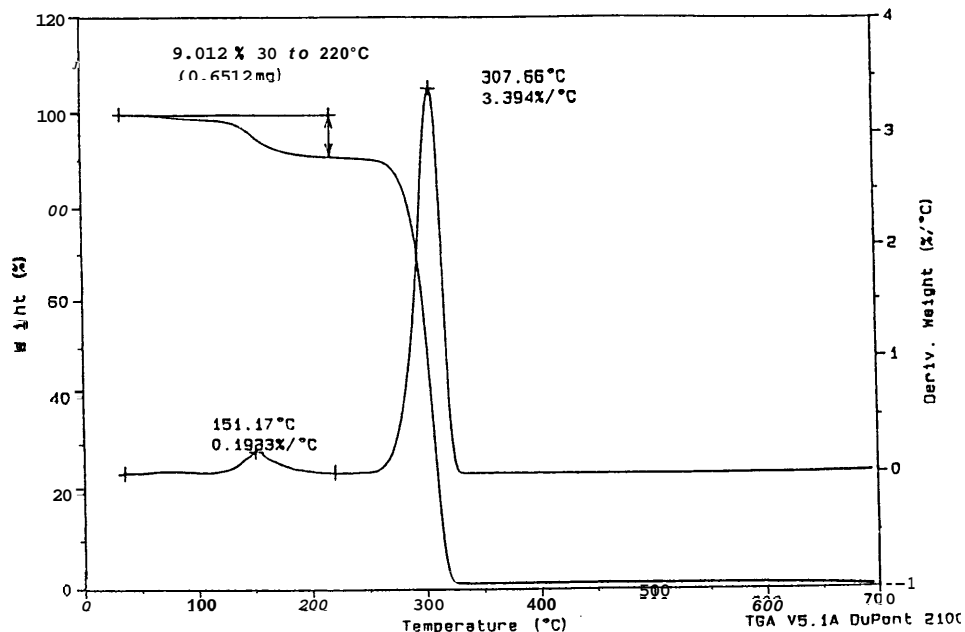


Figure 1. TGA of Polybromotrifluoroethylene ("PDBE")

With this fluorinated polymer, the cracking is complete (there is no significant char or other residue). Cracking occurs almost entirely at about 300°C (about 550° F); some small amount of pyrolysis is observed above 150°C, but this may be due to absorbed water (water vapor was observed in the infrared spectrum; the cracking product was identified as the monomeric bromotrifluoroethylene building block, on the basis of the infrared spectrum). These conditions indicate reasonably high shelf stability at ambient temperatures and an ability to degrade at low fire temperatures.

RESULTS OF CURRENT PROJECT WORK:

ADDITIONAL POLYMERIC NVP AGENTS WITH EFFICIENT PYROLYTIC DECOMPOSITIONS

The following agents have been synthesized and shown by TGA to exhibit excellent pyrolytic decomposition:

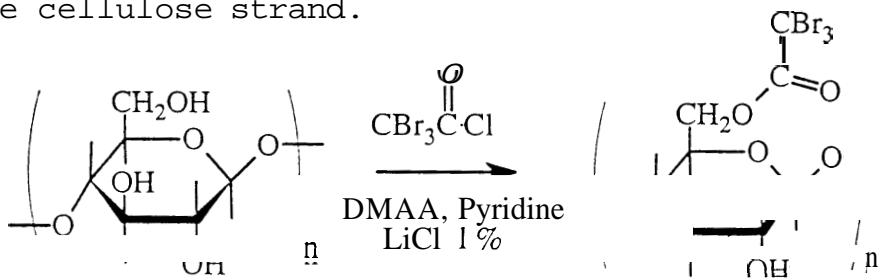
Cellulose Tribromacetate

Polvinyltribromoacetate

Poly[1,4-(2,2,3,3,tetrabromobutane)oxalate]

1. Cellulose Tribromacetate

This agent was prepared by acylation of cellulose in dimethylacetamide. The tribromoacetate moiety is quite bulky, and as a result the degree of substitution for this agent was only about 20%; the most likely point of substitution on the cellulose moiety would be at the #6 carbon, since this location poses the least steric hindrance of the three available hydroxy groups in each of the glucose components of the cellulose strand.



Degree of Substitution = 20%

Despite the low degree of substitution, excellent pyrolytic decomposition was seen in the TGA; see Figure 2. (The pyrolysis also resulted in some charring as a result of decomposition of the glucose carbohydrate moiety.)

Sample: CELLULOSE BROMOACETATE
 Size: 6.2300 mg
 Method: 20 °C/MIN
 Comment: UNDER NITROGEN

TGA

File: C:CBRAC.001
 Operator: ARVIND
 Run Date: 17-Apr-96 15:52

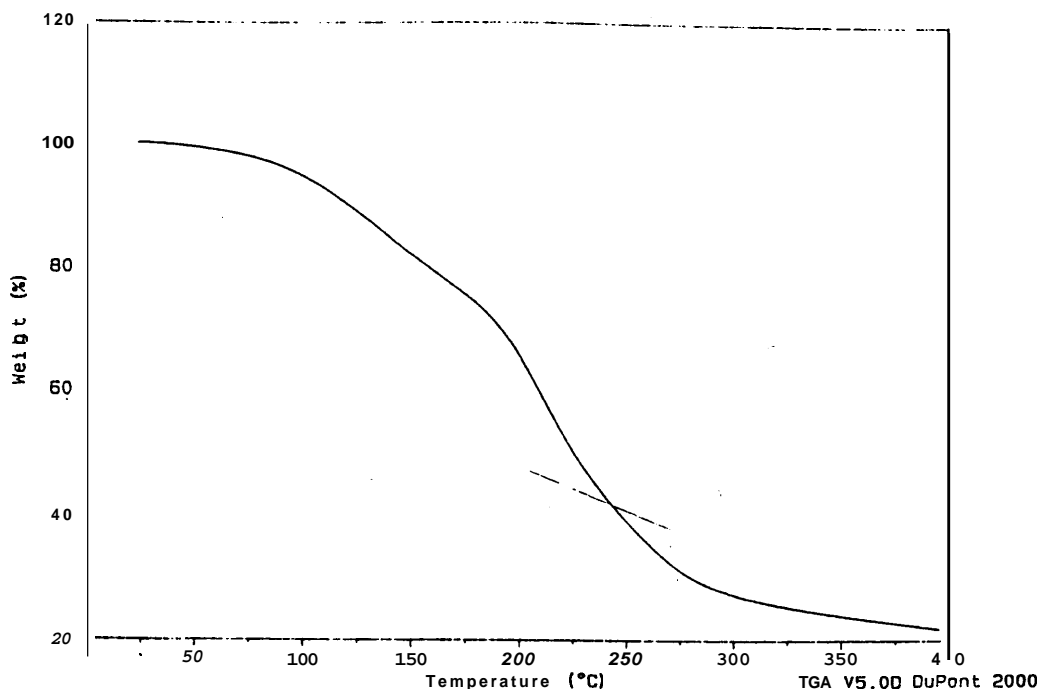
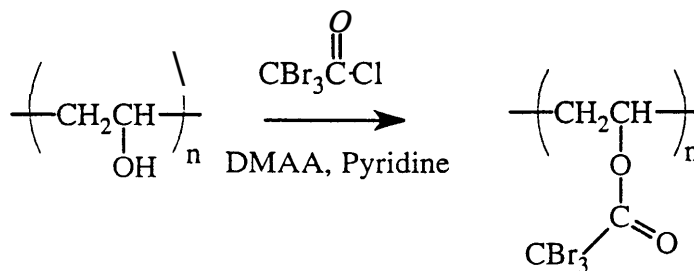


Figure 2. TGA of Cellulose Tribromoacetate

2. Polvinyl Tribromoacetate

This agent was prepared by acylation of polyvinyl alcohol by tribromacetyl chloride in dimethylacetamide. Despite the steric requirements of the bulky tribromoacetate, the polyvinyl backbone is considerably more open to substitution than is the case for cellulose; accordingly, the degree of substitution for this agent was found to be in excess of 50%. As will be discussed later in this presentation, work is in progress for synthesis of the monomeric vinyl tribromoacetate; it is anticipated that polymerization of this monomer will result in a very high degree of substitution.



Degree of Substitution = 50%

Again, excellent pyrolytic degradation was noted in the TGA, with little or no charring observed. (See Figure 3.)

Samp 1e: PVBrAc
 Size: 13.7700 mg
 Method: 10 °C/MIN
 Comment: TO CHECK DEG. TEMP.

TGA

File: C:\TGAPVBAAC.1
 Operator: SHIVSHANKAR/RAJESH
 Run Date: 21-Apr-96 22:13

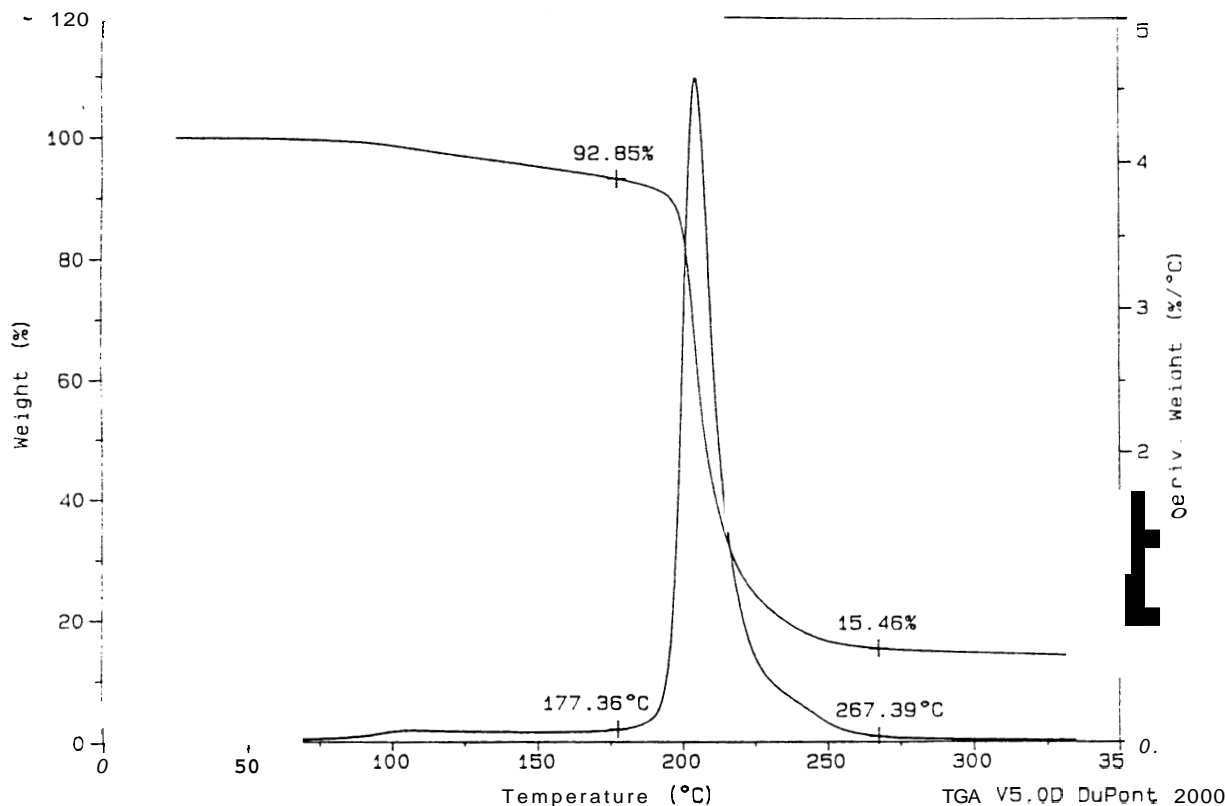
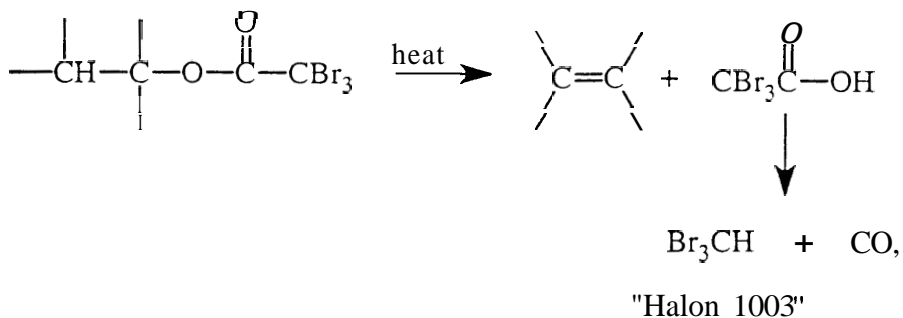


Figure 3. TGA of Polyvinyl Tribromnoacetate

For both the cellulose and polyvinyl agents, the mode of thermal decomposition is postulated as involving the following general mechanistic pathway:

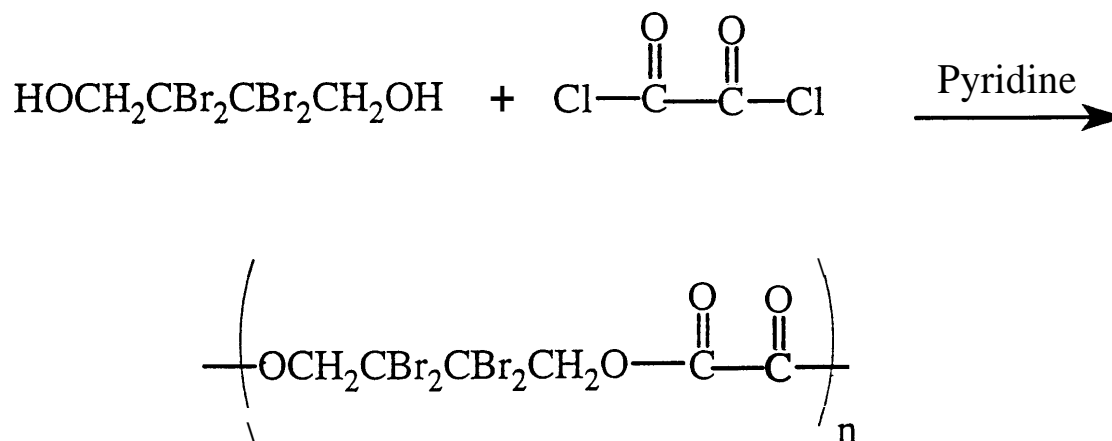
MODE OF PYROLYSIS



By using dibromofluoroacetyl chloride as the acylating agent, the resulting dibromofluoroacetyl group would be expected to produce CFBr_2H (Halon 1102), which has been shown to be an excellent HBFC extinguishing agent. As will be discussed later in this presentation, we intend to pursue this synthesis.

3. Poly[1,4- (2,2,3,3,tetrabromobutane)oxalate]

This agent was prepared by condensation polymerization of 2,2,3,3-tetrabromo-1,4-butanediol with oxalyl chloride:



Again, excellent pyrolytic degradation was noted in the TGA, with little or no charring observed. (See Figure 4.)

Sample: POLYOXALATE
 Size: 11.1380 mg
 Method: 10 °C/MIN
 Comment: TG

TGA

File: C:\POXOLATE.000
 Operator: ARVIND
 Run Date: 25-Apr-96 10:08

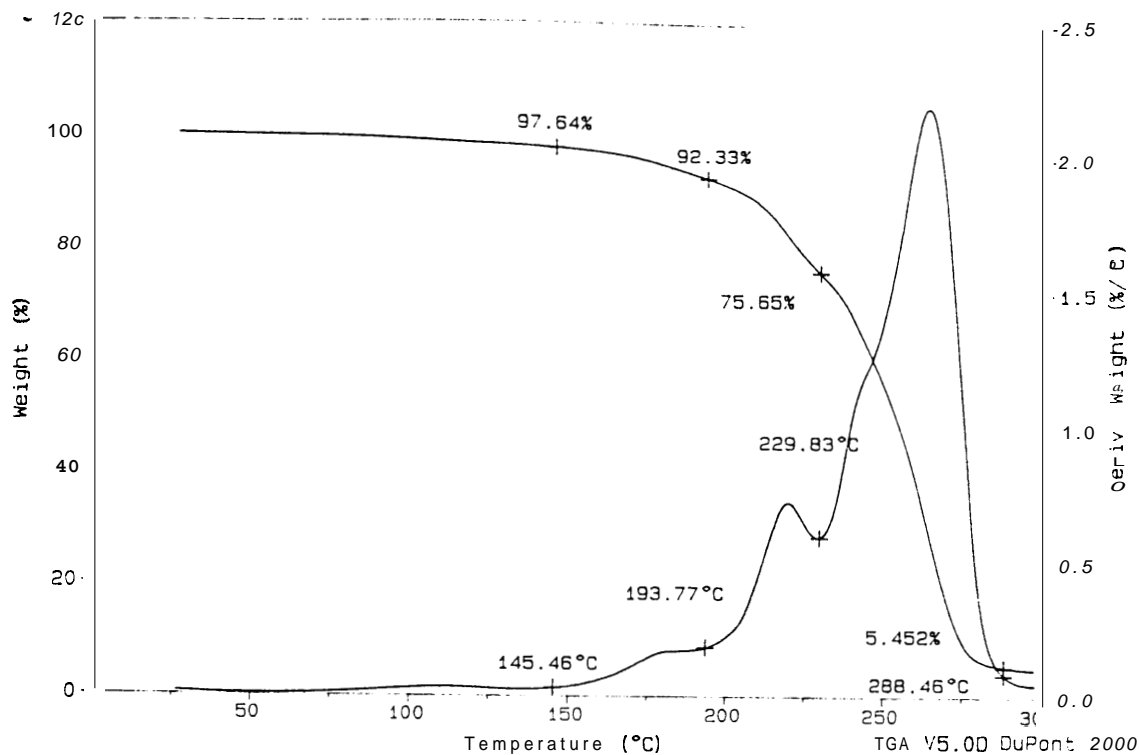
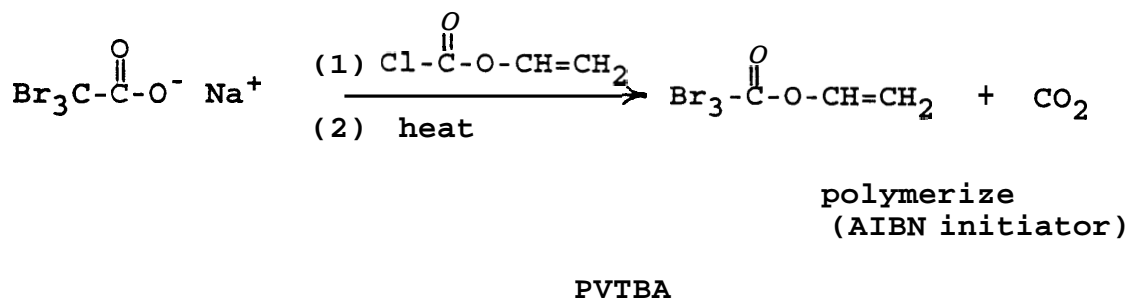


Figure 4. TGA of Poly[1,4-(2,2,3,3-tetrabromobutane)oxalate]

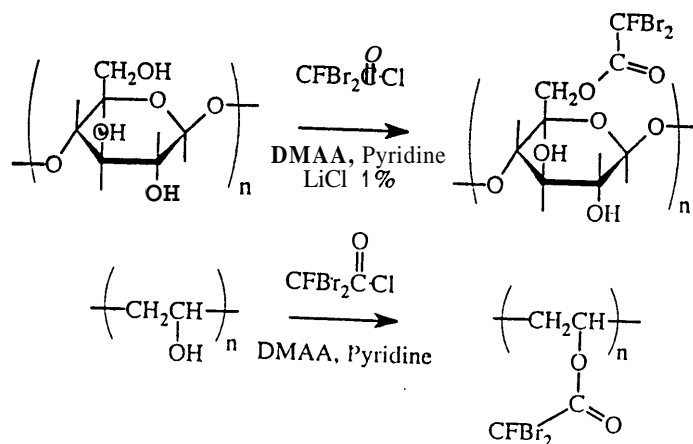
WORK IN PROGRESS

ALTERNATIVE SYNTHESIS OF POLYVINYLTRIBROMOACETATE (PVTBA)



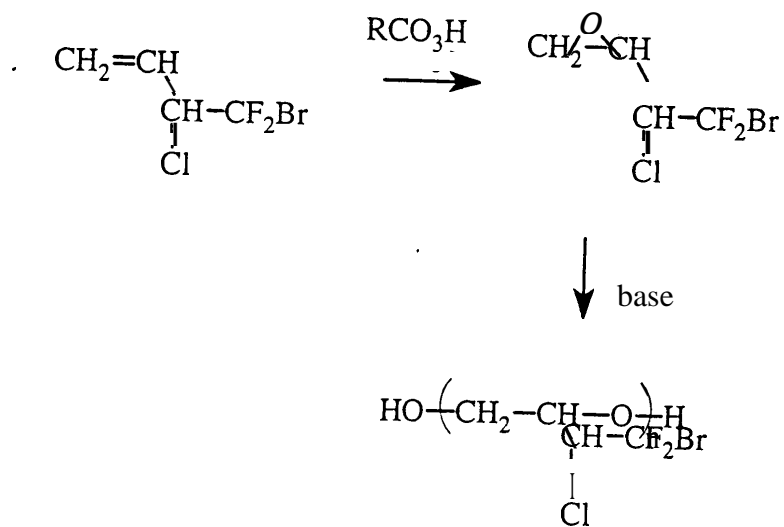
INCORPORATION OF DIBROMOFLUOROACETYL GROUPS IN POLYESTERS

E.G.,

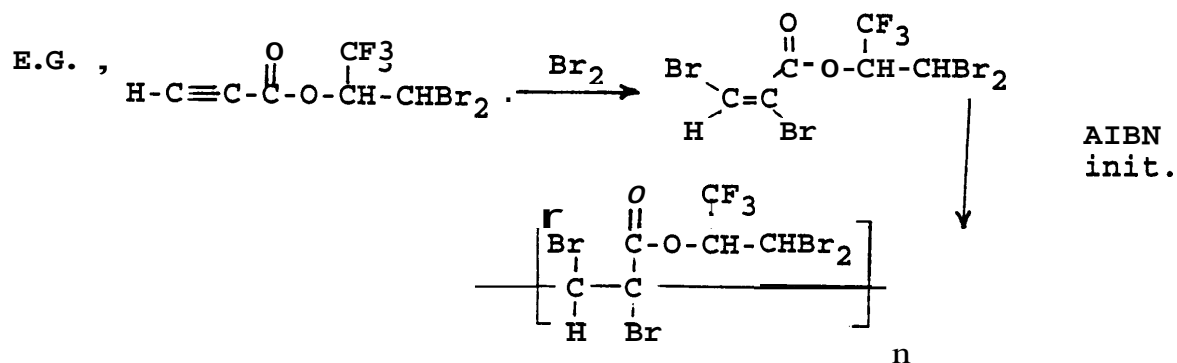


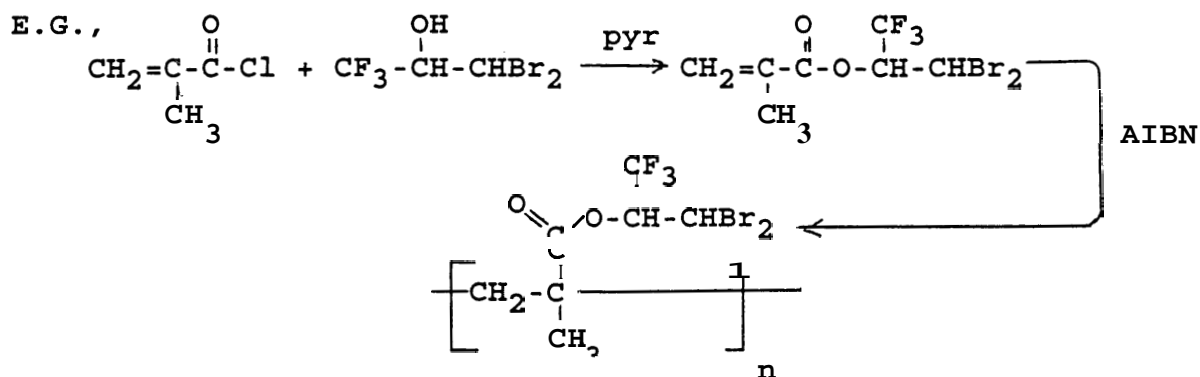
POLYETHERS

E.G.,



OTHER POLYVINYL ESTERS





PROBLEM AREAS

From the standpoint of determination of fire extinguishing capabilities, a good analog of the cup burner testing apparatus developed at NMERI and elsewhere is needed for bench scale evaluation of these solid NVP agents. In preliminary "waste basket" fire extinguishment tests, PBTFE proved effective in extinguishment. This type of testing is highly subjective, however. (The monomeric bromotrifluoroethylene which was identified as being the sole product of cracking of PBTFE was tested using the NMERI cup burner apparatus at Tyndall AFB, and was shown to be comparable in effectiveness to the Halons and for CF_3I .)

Preliminary toxicity testing was performed over a five week period, with PBTFE being 'fed to gold fish in water with techniques established for preliminary evaluation of other firefighting agents. No deleterious effects on the fish were noted. Based on analogies with other innocuous polymers (e.g., polystyrene, polyvinyl chloride, polyvinylidene chloride, etc.) formed from mutagenic/carcinogenic/toxic monomers, it might be anticipated that toxic effects of the NVP polymeric agents might be equally benign. It is obvious, however, that much more complete toxicology studies need to be performed.

Pending successful development and completion of bench scale means of evaluation of NVP agents, and determination of non-toxic effects of these agents, large scale field tests could then be performed to establish the efficacy of any NVP agent system.

SIGNIFICANCE OF RESULTS

NVP agents have greatly reduced ODP, GWP and toxic vapor properties, and pose greatly reduced atmospheric emissions due

to fire extinguishing operations or from accidental releases. Agent requirements for firefighting operations would be greatly reduced, in comparison to conventional agents, most of which evaporate en route to a fire when delivered as streaming agents. Greatly extended throw ranges would result in increased safety for firefighters, since NVP agents can be projected from much greater distances. This improved agent system may be beneficial in terms of optimizing usage of Halon streaming agents in the Halon Bank. NVP agents can be incorporated into fire preventative paints and resins which will release Halon agents upon exposure to high heat.

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